

Hole and Electron Bands in n-type CdCr_2Se_4

Abstract: A phenomenological model is presented to explain the anomalous temperature dependencies of the electrical resistivity and the Hall and Seebeck coefficients of indium-doped CdCr_2Se_4 with selenium deficiencies. The model postulates the existence of a hole band below localized donor levels, well above the intrinsic valence band. The assumed relative motions of the hole band and the donor level as the temperature is lowered, together with the optically deduced downward motion of the conduction band, are adequate to explain the data in a consistent manner. It is hypothesized that the hole band as well as the donor levels are related to the combination of indium ions and selenium deficiencies.

The chalcogenide spinel CdCr_2Se_4 is a semiconductor which becomes a ferromagnet below $T_c = 130^\circ\text{K}$.^{1,2} The Cd (Group II) atoms are situated on the crystallographic A sites. When some of them are replaced by In (Group III) atoms, the latter act as donors and the material becomes n type; on the other hand, when the dopant atoms are Ag (Group I), the material becomes p type. Early measurements³ of electrical transport in Ag-doped and In-doped samples, gave indications of differences between the two which are more basic than just the types of conductivity extant. Since the In-doped samples exhibited much more interesting and unusual behavior, they were investigated in greater detail, and they are the only ones with which the present paper is concerned.

Measurements of the electrical resistivities ρ , the normal Hall coefficients R_0 and the Seebeck coefficients Q were reported on a series of non-stoichiometric⁵ (Se-deficient) samples of $\text{Cd}_{1-x}\text{In}_x\text{Cr}_2\text{Se}_4$ between 4.2°K and 300°K .⁶ The coefficients R_0 and Q were always negative. The results were anomalous, in that no model which was based on electrical transport in a single conduction band (or even two conduction bands of s and d character) could explain the seemingly contradictory temperature dependencies of ρ and R_0 on the one hand, and of Q on the other. This was the case even after effects of spin-disorder scattering⁷ on Q as well as spin splitting of the conduction band⁸ were taken into account. The experimental data for the sample, wherein $x = 0.01$, are shown in Fig. 1, which contains ρ and R_0 , and Q . From 300°K down to

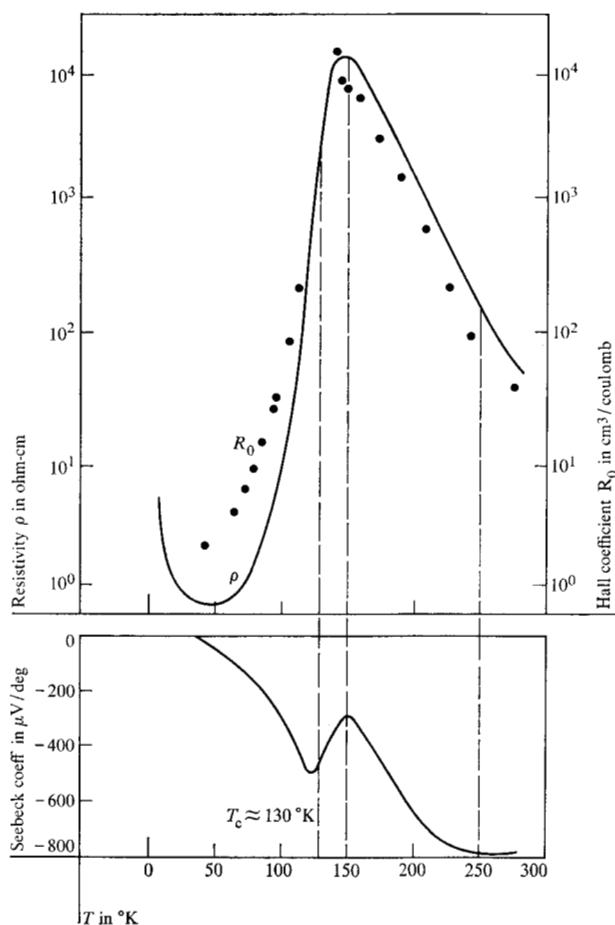


Figure 1 Temperature dependencies of the electrical resistivity ρ , the normal Hall coefficient R_0 , and the Seebeck coefficient Q , of $\text{Cd}_{0.99}\text{In}_{0.01}\text{Cr}_2\text{Se}_4$.

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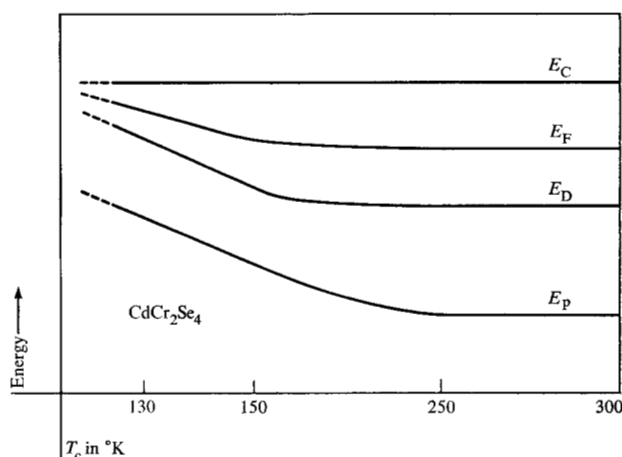


Figure 2 The relative motions of the Fermi level, the donor level, the hole band, and the conduction band with temperature.

150°K, ρ and R_0 indicate a decrease in the electron concentration, whereas $|Q|$ diminishes below 250°K, indicating just the opposite. Below 150°K ρ and R_0 indicate a very rapid increase in electron concentration, whereas $|Q|$ increases down to 125°K—which, again, is contradictory.

The simplest phenomenological model which accounts for these observations in terms of carrier density variations is one which invokes the simultaneous presence of conducting electrons and holes, the contribution of the latter being larger in the vicinity of 150°K, where ρ , R_0 and Q have their extrema. The postulated hole band which our model requires is a subsidiary band situated in the band gap. The model includes, then, a conduction band whose lower edge is E_C , a hole band whose upper edge is E_p , and localized donors situated at energy level E_D .

From 300°K down to about 200°K, plots of $\log \rho$ and $\log R_0$ vs T^{-1} yielded straight lines with activation energies of about 0.23 eV. The relevant statistics are in the "low-temperature, high-donor-concentration limit," in which case the Fermi level E_F lies very nearly half-way between E_C and E_D , whence we deduce that $(E_C - E_D) \approx 0.46$ eV. As the temperature is lowered further below 200°K, both ρ and R_0 continue to increase, but with diminishing rates, until they turn around at 150°K. Analysis of the model further requires that the following inequality obtain at all temperatures:

$$E_F > \frac{E_C + E_p}{2} \quad (1)$$

Since E_F is approximately half-way between E_D and E_C , the inequality means that the hole band always lies below the donor level. An additional condition which must be fulfilled at 150°K is that the electron and hole concentra-

tions go through extrema; i.e.,

$$\frac{d}{dT} \left(\frac{E_F - E_p}{kT} \right) = \frac{d}{dT} \left(\frac{E_C - E_F}{kT} \right) = 0. \quad (2)$$

From Fig. 1 we conclude that as T is lowered from 300°K, a freeze-out of electrons onto the donors takes place; however, as T goes below 150°K, a rapid increase in the electron concentration occurs. Although such behavior requires rather uncommon temperature dependencies of the various levels, it is known from optical measurements⁹ that the distance between the conduction band and the valence band edge decreases below 190°K from 1.37 eV to about 1.16 eV at 20°K. The fastest rate is near T_c . The relative motions of E_C , E_F , E_D and E_p which are required to explain the transport data are shown schematically in Fig. 2. From 300°K down to about 250°K, $(E_C - E_D)$ remains constant. From there to lower temperatures, $(E_F - E_p)$ decreases until, at 150°K, E_p is close to E_D and to E_F so that the hole contribution is greater. At this temperature, the hole contribution to Q cancels a large part of the electron contribution to Q . In the vicinity of 150°K, E_D and E_p move apart, or at least do not continue to approach each other, so that the contribution of E_p diminishes as T decreases further. The donor level at E_D is now tied to E_p rather than to E_C , so that as E_C moves down rapidly, the ionization energy of the donors decreases, resulting in an increase in the electron concentration.

At this juncture we can but speculate about the atomic origin of the proposed hole band, and indeed about the donors themselves. As was mentioned earlier, the measurements were done on In-doped samples which were known to have Se deficiencies.⁵ Measurements on stoichiometric samples yield quite different results. For example, a sample in which the In content was 0.027 atomic percent, but which did not have Se deficiencies, had a room-temperature resistivity about four orders of magnitude larger than a similar non-stoichiometric sample, and a positive Q . Furthermore, the activation energy between 300°K and 200°K was 0.66 eV, which is approximately half the intrinsic band gap. The resistivity did not exhibit a maximum at 150°K but continued to rise monotonically with decreasing T . The conclusion is that the n-type character of the indium-doped compound depends not only upon the presence of the indium, but concomitantly upon the presence of selenium deficiencies. In particular, from the above, it is suggested that the donor centers are the selenium deficiencies. It is also suggested that the postulated p band is a more than half-filled impurity band arising from the overlap of wave functions localized on indium sites. Such a band is assumed to lie lower than the donor level and is more than half-filled as a consequence of the additional carriers associated with the selenium deficiencies.

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4. At low temperatures (30°K to 100°K), R_0 was obtained from the high-field slope of the Hall voltage. At high temperatures ($T > 150^\circ\text{K}$), it was obtained from the low-field slope. A plot of R_0 vs the susceptibility χ in the paramagnetic regime was strongly non-linear, consistent with a temperature-dependent Hall effect. [See J. J. Rhyne, *Phys. Rev.* **172**, 523 (1968) and S. von Molnar and T. Kasuya, *Phys. Rev. Letters* **21**, 1757 (1968)].
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